**Ocean Science
Discussions**

Interactive comment on "A chemical ionization mass spectrometer for continuous underway shipboard analysis of dimethylsulfide in near-surface seawater" *by* E. S. Saltzman et al.

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Author response to Anonymous Referee 2

Referee 2 made the same valid point about detection limits as did referee 1. Our response to referee 1 and the revised figures should help clarify that point. In response, we have also revised the paragraph in the manuscript on signal to noise to improve clarity and to remove some irrelevant comments about counting statistics. We added a note about the fact that the signal variance in the instrument tends to be first-order in DMS. In other words, there are sources of variability that are proportional to the magnitude of the signal being measured (temperature or gas flow rate fluctuations,

gas turbulence, mass spectrometer drift, etc.).

The revised paragraph will read as follows:

"The observed signal variability (1σ) in the laboratory calibration ranges from 37-90 ppt over the range of 10-35 ppb DMS. Signal variance tends to increase with increasing DMS signal (Figures 4 and 5). The most likely causes are gas flow rate fluctuations in the equilibrator or inlet, turbulence affecting ion transmission in the instrument, and mass spectrometer drift. Because field measurements involve the ratio of two measurements (at mass 63 and 66), the variance of an ambient DMS measurement is approximately twice that of either ion. Based on the laboratory data, we estimate an upper limit for the detection limit of 148 ppt (S/N =2). Under field conditions, the signal variance is slightly larger than in the laboratory. This increased instrument noise is most likely due to motion, thermal effects, or electrical noise (Fig. 6). Using the observed variability in the field data at a DMS level of 10 ppb, we estimate a detection limit of 220 ppt. Based on the seawater solubility, this would be equivalent to aqueous concentrations of 0.12 0.10, and 0.08 nM DMS at temperatures of 15, 20, and 25oC."

Reviewer 2 commented correctly that at lower seawater temperatures, the water vapor content of the equilibrated gas stream is reduced, and the sensitivity of the instrument can be lower. Thus it is not technically correct that the detection limit would be constant at different sea surface temperatures as implied by the preceding paragraph. The reviewer is quite correct that this effect could be overcome by intentionally humidifying the air stream used to dilute the sample, although this was not done on this campaign. The magnitude of this effect is best assessed operationally with field data. This effect was demonstrated by Marandino et al. (2004), using a different instrument with similar ion chemistry. We have examined the field data from this study and will add a comment to the paper, as follows:

it "Under field conditions, the instrument response may vary as a function of sea surface temperature, as a result of changes in water vapor level in the analyzed gas stream.

This is due to the fact that water vapor affects the abundance of H3O+ in the ion source. During the field deployment described below, instrument sensitivity increased by about 10

Reviewer 2 raised a question about whether the porous membrane might influence the apparent solubility of DMS in the equilibrator. The membrane is an open structure that allows gas to diffuse directly through the pores without having to pass through the PTFE itself. As long as the rate of exchange of the gas across the open pores is much larger than the permeability across the solid PTFE, the presence of the membrane should have little affect on the DMS level on the gas phase side of the membrane. Typical gas phase molecular diffusion coefficients in air are on the order of 0.1-0.2 cm2/s, while that for gases in PTFE are on the order of 10-7 cm2/s (Pasternak et al., 1970). Even considering that tortuosity slows the gas phase diffusion through the pores compared to diffusion in free air, the diffusion through the solid is likely to be insignificant compared to that through the pores.

It is true that the PTFE membrane itself will equilibrate with seawater DMS. As DMS levels and temperatures vary, DMS will dissolve and exsolve from the polymer. We have not found a measured solubility of DMS in PTFE, but based on literature data for other gases, one might expect it to be several-fold greater than that in water (Pasternak et al., 1970). Even assuming the solubility to be 10-fold greater in PTFE than in seawater (likely an overestimate), the amount of DMS residing in the membrane is small. The total mass of PTFE in the equilibrator is approximately 1 cm3, and the seawater flow rate is 33 cm3 s-1. When saturated under these conditions, the membrane would contain roughly as much DMS as flows through the tubing in 0.3 s.

Reviewer 2 suggested that we measure the DMS solubility in the same setup used for detection. This could be done, but high precision solubility measurements take some care and more time than we currently have. We think it likely, for the reasons mentioned above, that DMS solubility measurements would yield results similar to those measured with traditional methods. We have used a similar system to measure the solubility

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of methyl bromide (De Bruyn et al., 1977), and obtained reasonable agreement with previously published studies. In the case of methyl bromide (a more soluble gas than DMS), there were 6 comparison points from the literature that differed from our data by 0.9

Technical corrections:

Reviewer 2 raised a question about the reaction formula on p. 1572: "To both sides of formula 1 "N2" is added. I presume this should have been "Ni", to indicate the site of protonation?" Protonation and clustering of water in the ion source occurs in the gas phase, and the Ni foil is not represented in the reaction shown. In its forward direction, the clustering reaction involves the production of a single product from two reactants. Conservation of angular momentum requires that a third body be present to stabilize the intermediate.

p. 1579, last line: Shouldn't the "63/66 ratio" be changed in: "66/63 ratio" as in figure 5? That was an error, and will be corrected in the final revised manuscript.

Revised Figure:

In our response to Reviewer 1 we revised Figure 4 to show 1 minute averaged signals in the laboratory calibration. An updated version of Figure 5 showing the results of that calibration using the averaged data is attached here. Using the averaged data, the standard deviation of the measurements is considerably reduced.

Fig. 1.

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